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Modelling sorption of ciprofloxacin using the ASM-X framework – Evaluation of factors influencing activated sludge treatment and implications on environmental risk assessment

Fabio Polesel*[1], Kai Lehnberg[2], Wolfgang Dott[2], Stefan Trapp[1], Kevin V. Thomas[3], Benedek Gy. Plósz[1,3]

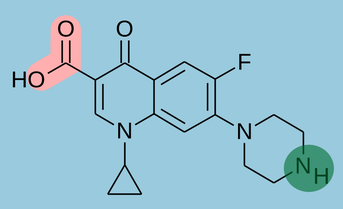
[1]Department of Environmental Engineering, DTU, Kgs. Lyngby, Denmark; [2]Institute of Hygiene and Environmental Medicine, RWTH Aachen University, Aachen, Germany; [3]Department of Ecotoxicology and Risk Assessment, NIVA, Oslo, Norway;

*fabp@env.dtu.dk

1. Introduction

Ciprofloxacin:

- ~ 1 t/a in Nordic countries [1][2]
- Highly **toxic** to cyanobacteria [3]
- **Zwitterionic** (pK_a=6.16, 8.63) [4]



Fate in wastewater

Ciprofloxacin is mostly removed from sewage via **sorption to activated sludge** [5]. Its relatively high sorption capacity was found to be the result of **electrostatic interactions** with solid matrices – e.g., cation bridging [6].

Case study

Systematic reduction of removal of ciprofloxacin in Bekkelaget WWTP (Oslo, Norway) [7]

Hypothesis

Reduced elimination caused by decrease of sorption capacity

Objective of the study

To investigate how

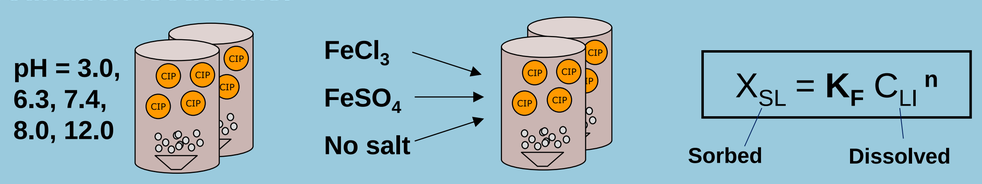
- **pH conditions**
- **salt dosing for P removal**

affect sorption of ciprofloxacin on activated sludge by using

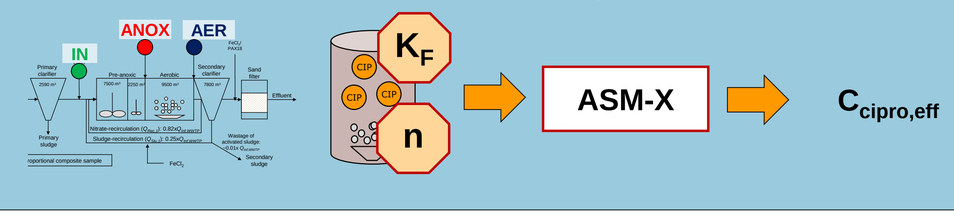
1. **Batch experiments**
2. **Full-scale fate (ASM-X)**

2. Methods

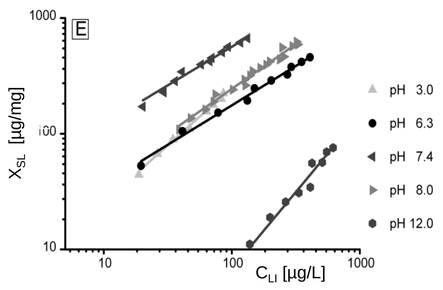
1) Targeted batch experiments were performed to evaluate **sorption onto activated sludge** under different **pH** and **iron salt dosing** conditions using **Freundlich isotherms.**



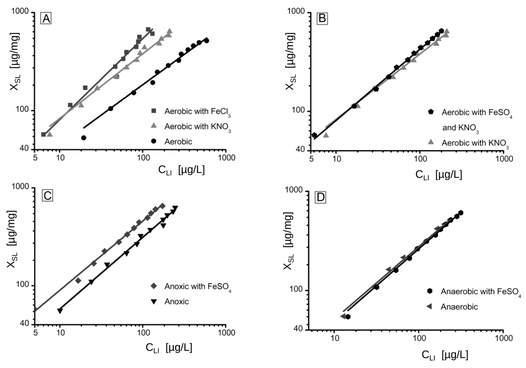
2) The **A**ctivated **S**ludge **M**odel for **X**enobiotics **– ASM-X** ([7]) was used to predict measured ciprofloxacin's concentrations at Bekkelaget WWTP (Oslo). **Freundlich parameters** estimated in batch were used for **ASM-X calibration**. **Effluent concentrations** of ciprofloxacin ($C_{cipro,eff}$) could also be estimated.



3. Results – pH and iron effect

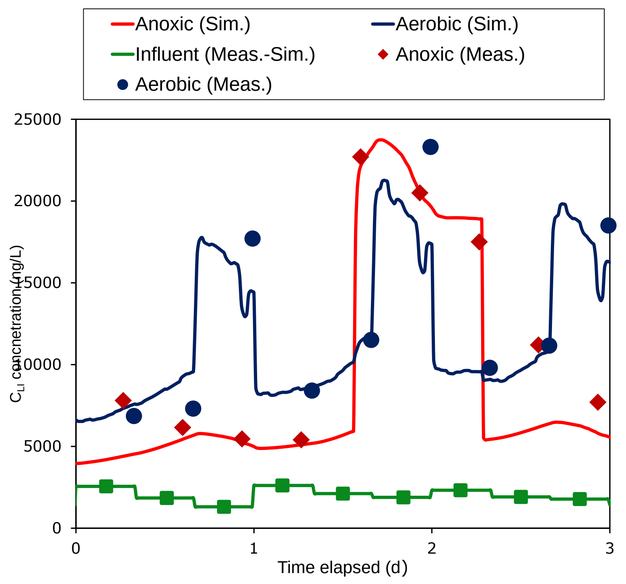


- **Maximum sorption at pH=7.4**, ~ isoelectric point. **Zwitterions** had highest sorption capacity (via bound cations on sludge)
- **Anions** (pH=12) had negligible sorption capacity, possibly due to repulsion to sludge [8]



- **Increase** of sorption by spiking **iron salts** (except for anaerobic exp.), with possible **complexation**
- Redox conditions affected sorption only in the presence of iron

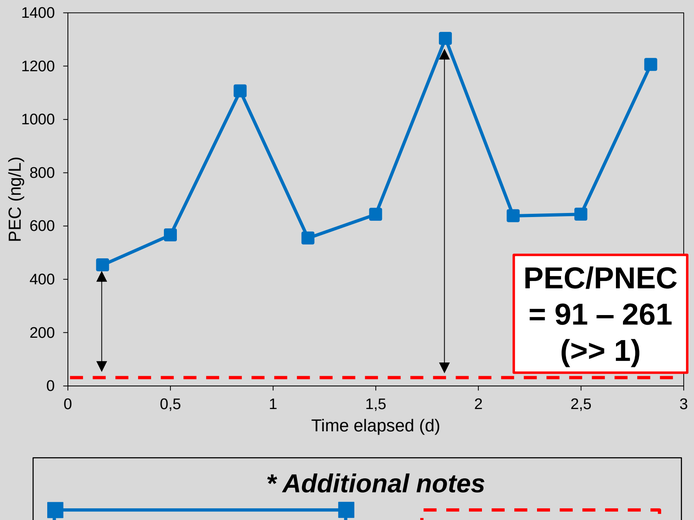
4. Full-scale simulations



Intermittent ciprofloxacin's removal (C_{LI} > 15 µg/L) occurred in Bekkelaget full-scale WWTP and was associated to **sorption deterioration** [7].

Full-scale simulations using batch-estimated Freundlich parameters showed that **pH increase (> 8) was more likely to have caused reduced removal.** No specific effect could be associated to the reduction in salt dosing (usually occurring in night hours).

5. Implications for risk assessment



PECs (*) of ciprofloxacin, calculated by using a dilution factor **DF=10**, varied of a **factor of ~ 3** over the sampling period, as a result of **changes in sorption capacity**.

In general, **PECs were 2 orders of magnitude higher than PNECs.** A situation of **potentially high risk** was therefore identified for Bekkelaget, with regard to release of **ciprofloxacin.** Similar evidences were obtained by [1].

**** Additional notes***

PEC = $C_{cipro,eff}$ / DF

Predicted **E**nvironmental **C**oncentration

PNEC = 5 ng/L

Predicted **N**on-**E**ffect **C**oncentration

6. Conclusions

- **When present as zwitterion in solution, ciprofloxacin was found to sorb at a higher extent as compared to other ionic species. Presence of iron salts increased sorption extent under aerobic and anoxic conditions.**
- **Full-scale simulations with ASM-X associated the intermittent removal of ciprofloxacin in activated sludge to a pH increase in the biological reactors, rather than to the reduction in iron salt dosing regimes.**
- **Predicted environmental concentrations (PECs) of ciprofloxacin had evident time variations, as a result of dynamic loading and operational conditions typical to WWTPs. Potentially high risk, due to high PECs of ciprofloxacin, was associated to the water bodies, receiving Bekkelaget WWTP effluent.**

References:

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